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PB-281 529

Partial Characterization of Chlorinated Organics in Superchlorinated Septages and Mixed Sludges

Municipal Environmental Research Lab, Cincinnati, Ohio

Mar 78

PB 281 529

EPA-600/2-78-020
March 1978

Environmental Protection Technology Series

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TECHNICAL REPORT DATA
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1. REPORT NO. EPA-600/2-78-020	2.
3. RECIPIENT'S ACCESSION NO. PB281529	
4. TITLE AND SUBTITLE: Partial Characterization of Chlorinated Organics in Superchlorinated Septages and Mixed Sludges	5. REPORT DATE: March 1978 (Issuing Date)
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): Robert H. Wise, Thomas A. Pressley, and Barry M. Austern	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Municipal Environmental Research Laboratory--Cin.,OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	10. PROGRAM ELEMENT NO. 1BC611 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS: Same as above	13. TYPE OF REPORT AND PERIOD COVERED: Inhouse Report 2/10/77-6/24/77 14. SPONSORING AGENCY CODE: EPA/600/14

15. SUPPLEMENTARY NOTES

Project Officer- Robert H. Wise 513/684-7627

16. ABSTRACT

The chlorinated organic materials produced by applying the proprietary Purifax process to a septage and a mixed primary/secondary sludge were studied to assess the types, amounts, and distribution of chlorinated organics present. Total organic chlorine in the solids phases was determined by Schöniger-flask combustion. Concentrated hexane-ether extracts of the liquid phases were also analyzed for total organic chlorine by microcoulometric titration; these same extracts were then analyzed by GC/MS for individual organic compounds. Helium-purgeable organics in the liquid phases were also determined by GC/MS. Liquid phases from one Purifax installation were analyzed for TOC, TDS, and TSS to furnish engineering cost data for applying filtration/carbon adsorption as a Purifax-treatment adjunct.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Sludge disposal Sludge Septic tanks *Chlorination *Chemical analysis *Chemical Composition	*Purifax Process *Superchlorination Septages Sludge treatment Septage treatment *Sludge analysis *Septage analysis	13B

18. DISTRIBUTION STATEMENT: RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)*: UNCLASSIFIED	21. NO. OF PAGES: 30
	20. SECURITY CLASS *(This page)*: UNCLASSIFIED	22. PRICE: A03-A01

EPA Form 2220-1 (9-73)

☆ U.S. GOVERNMENT PRINTING OFFICE 1978-757-140/6810 Region No. 5-11

EPA-600/2-78-020
March 1978

PARTIAL CHARACTERIZATION OF CHLORINATED ORGANICS IN SUPERCHLORINATED SEPTAGES AND MIXED SLUDGES

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution, and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for preventing, treating, and managing wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for preserving and treating public drinking water supplies, and for minimizing the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and is a most vital communications link between the researcher and the user community.

This report describes the results of an analytical study performed on sludges and septages that were chemically stabilized with the proprietary Purifax superchlorination process. The superchlorination process is a technological solution to the problem of sludge bio-instability. Knowledge of the end products of the superchlorination provides insight into potential environmental impacts from the sludges and wastewaters discharged from the superchlorination process.

Francis T. Mayo
Director
Municipal Environmental
Research Laboratory

ABSTRACT

The chlorinated organic materials produced by applying the proprietary Purifax process (i.e., stabilization by superchlorination) to a septage and a mixed primary/secondary sludge were identified in both the solid and liquid phases to assess the types, amounts, and distribution of chlorinated organics present.

Total organic chlorine concentrations of the solid phases were determined by Schöniger-flask combustion techniques. Total organic chlorine concentrations for concentrated hexane-ether extracts of the liquid phases were determined by microcoulometric titration. These same concentrated hexane-ether extracts, as well as the helium-purgeable "volatile" organics from the unextracted liquid phases, were then analyzed by gas chromatography/mass spectrometry. Analyses for total organic carbon, total dissolved solids, and total suspended solids were also performed on the liquid phases from one location to furnish engineering data for assessing both the feasibility and cost of applying filtration/carbon adsorption as an adjunct to Purifax treatment.

The amounts of organic chlorine found in the Purifaxed solids were relatively large (1% by weight); however, the identities of these compounds remain unknown because of analytical limitations. The specific compounds identified in the liquid phases do not, by themselves, eliminate superchlorination as an environmentally acceptable process these compounds (except in lower concentrations) are the same types as those presently found in contaminated surface waters. Still lacking is information about chlorinated gaseous organics released to the atmosphere when Purifaxed materials are discharged from the reactor.

This report covers a period from February 1977 to July 1977, and work was completed as of August 1977.

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ACKNOWLEDGMENTS

We gratefully acknowledge the cooperation of Ray Thompson, Chief, Surveillance & Analysis Division, Region I (EPA), and the Plainfield, Connecticut, Wastewater Treatment Plant personnel, who cooperated to furnish the samples of mixed primary/secondary sludges.

We are also indebted to Robert Miele and Kieran Bergin of the Los Angeles County Sanitation Districts and to Joseph Borgerding of the Ventura County Regional Sanitation District for furnishing the samples of Ventura septages used in this study.

SECTION 1

INTRODUCTION

The proprietary Purifax process is one of several systems able to stabilize and disinfect sludges or septage before land disposal. When required, it also is used to treat anaerobic digester supernatant. Briefly, the Purifax process is a method developed by BIF (a unit of General Signal Corporation) for superchlorinating concentrated biological wastes (for example, sludges and septages) to stabilize the active solids biologically and thus enhance their dewatering characteristics. Competing processes for the sludge treatment function include lime stabilization, heat treatment, wet air oxidation and anaerobic digestion. Lime and polymer treatment with air stripping of ammonia is an alternative for treatment of digester supernatant. The Purifax process, as currently practiced with chlorine costs of typically $12/ton of treated sludge, is competitive with the alternative treatment processes.

The very high concentrations of chlorine (approximately 700 to 3,000 mg/l) typically employed during the Purifaxing of septages and sludges are also capable of producing chlorinated organics. Limited analytical results on chlorinated organics from Purifaxed septages have already been reported by Mashni (1). Before Mashni's work, the engineering firm of Metcalf and Eddy (2) reported their analytical studies of five different waste streams, each taken from a different geographical location. All of those waste streams were being routinely subjected to Purifax treatment at the time samples were taken. The specific compounds of interest to Metcalf and Eddy were nine chlorinated herbicides (including 2,4-D and 2,4,5-T), five chlorinated insecticides, and polychlorinated biphenyls. Rather than producing any of these objectionable compounds, Purifaxing actually seemed to lower their concentrations in most instances. Since that time, the volatile organics analysis method of Bellar and Lichtenberg (3) has been reported, and computerized gas chromatograph/mass spectrometer (GC/MS) systems have become widely available. This, in turn, has led to the discovery that waters and wastewaters often contain a far greater variety of undesirable chlorinated organic contaminants than those studied by Metcalf and Eddy, especially when organically contaminated aqueous waste streams are deliberately chlorinated for disinfection or waste stabilization.

The present study of Purifaxed wastes was performed to determine what types of chlorinated organics are thus produced, how such compounds are likely to be discharged (that is, primarily as constituents of the solids phase, the liquid phase, or both) and, in each case, how much. With the information thus obtained, at least a tentative evaluation of the environmental risks associated with this process is possible.

SECTION 2

CONCLUSIONS

Purifaxed samples of one septage and one mixed primary/secondary sludge were each separated into solids and liquid phases, then analyzed for their organic contents by a variety of different techniques.

Both solids fractions contained 0.9% to 1.0% total organic chlorine, based on dry weight. No attempt was made to identify individual organic constituents in these relatively insoluble solids.

Hexane-ether extracts of both liquid fractions assayed approximately 100 to 200 µg/l of total organic chlorine, or less than 1% of the total organic contents of the unextracted liquid phases. GC/MS analyses, both of the hexane-ether extracts and of the helium-purgeable, volatile organics in the unextracted aqueous phases, yielded slightly higher concentrations of the same kinds of organic compounds that are typically present in U.S. water supplies. A notable exception, however, was the highly toxic cyanogen chloride, present in all of the unextracted Purifaxed liquid phases in concentrations reaching 900 µg/l.

The centrate from Ventura contained approximately 200 mg/l of TOC, and less than 1 mg/l of this TOC was identified as specific organic molecules. The unidentified TOC is non-volatile and non-extractable and therefore cannot be analyzed by GC/MS methods. The amounts of chlorinated organics in that TOC are unknown.

Standards governing maximum permissible concentrations for the organic compounds found in the Purifaxed liquid phases have not yet been established for drinking water supplies and wastewater discharges. Environmental impacts of these molecules depend on site-specific dilution factors. Thus, Robert Tardiff of the Health Effects Research Laboratory in Cincinnati has indicated that the identified organics in the liquid centrates entering the environment do not by themselves constitute a basis for environmental unacceptability of the Purifax process (Personal communication).

Finally, the long-term environmental impact of the chlorinated organics in the Purifax solids placed in landfills or on soils are unknown. The organics are likely to include chlorinated proteins and amino acids, humic acids, carbohydrates, and fats. The toxicity of these chlorinated materials is unknown, but since the chlorinated sludge resists biodegradation, the chlorinated organics are probably biocidal (at least to bacteria).

The work carried out during this project does not represent a definitive study of chlorinated organic material produced by the Purifax treatment of septages and sludges. To carry out such a definitive study is beyond the current state-of-the-art and would require major-scale analytical resources (work space, trained manpower, time, and sophisticated analytical equipment) for analytical methods development.

SECTION 3

RECOMMENDATIONS

We recommend that no further direct chemical analyses of the solid or liquid phases be carried out at this time.

In the Purifax process, a gaseous phase is also discharged from the reactor, along with the solid and liquid phases. An analysis of this gas phase should be carried out.

Other fruitful approaches to this problem would include:

a) Controlled studies of the extent to which chlorinated material in Purifaxed solids is leached from landfills over extended periods of time.

b) Suitable toxicological studies (for example, animal feeding studies) to ascertain the occurrence and severity of any adverse health effects resulting from the chlorinated material in Purifaxed liquids entering drinking water supplies.

c) Determinations of the extent of environmental persistence of chlorinated organics produced by the Purifax process; or, conversely, the rate at which such chlorinated organics are biodegraded in natural environments.

Naturally, approaches a and c would require considerable analytical support and extensive analytical methods development.

SECTION 4

EXPERIMENTAL PROCEDURES

SAMPLE SOURCES, PROCUREMENT, AND STORAGE

Original plans called for us to receive two samples from Region I: a superchlorinated septage, and a superchlorinated mixture of septage plus primary/secondary sludge. Because of severe winter snows throughout most of Region I from January through March of 1977, septage collections in that Region were brought to a standstill. When it became apparent that septage would not be available for an indeterminate period, arrangements were made for shipment of a Purifaxed primary/secondary sludge (plus a representative unchlorinated control) from the Plainfield (Connecticut) Wastewater Treatment Plant with the understanding that our septage samples probably would have to be obtained elsewhere.

Purifaxing was carried out on February 9, 1977, using 21.8 kg (48 lb) of chlorine to treat 15,369 l (4,060 gal) of mixed sludges (1,417 mg Cl/l). Typically, free chlorine residuals for the product leaving this reactor had averaged 300 mg/l. The Purifaxed sample was divided into two portions immediately after collection. One portion was packaged for shipment with its free chlorine content intact; this sample was labeled "chlorinated sludge." The other portion was allowed to stand 4 hours, then it was dechlorinated with sodium sulfite solution and also packaged for shipment. This sample was labeled "dechlorinated sludge." Because both Purifaxed samples had been biologically stabilized, they could be handled without any further need for sample preservation. The required control sample for this work (that is, an untreated portion of the raw sludge fed to the Purifax unit) was highly unstable; therefore, it had to be packed and shipped in an insulated container filled with ice. This control sample was labeled "raw sludge."

All three samples were sent by Federal Express and arrived at our laboratory less than 24 hours after shipment. All of these samples were immediately placed in a walk-in cold-room until they could be readied for analysis.

The Purifaxed septage needed for this study was obtained from the Ventura County (California) Regional Sanitation District. Their Purifax treatment facility was operated solely on a septage feed for this project. The applied chlorine dosage was about 800 to 1,000 mg Cl/l; 4 hours after Purifaxing, the free residual chlorine concentration had decreased to 90 mg/l.

Sampling, packaging, and shipping protocol for the Ventura samples was identical to that for the samples from Plainfield, except that the Ventura samples were labeled "chlorinated septage," "dechlorinated septage," and "raw septage" (that is, the chlorinated septage was shipped with its free residual chlorine content intact; the dechlorinated septage was treated with Na_2SO_3 solution 4 hours after Purifaxing; and the raw septage feed to the Purifax unit was shipped in an ice pack). These three samples, also received less than 24 hours after shipment, were immediately stored in a cold-room.

All the chlorinated samples were tested (qualitatively) for free residual chlorine approximately 48 hours after Purifaxing. No remaining free residual chlorine could be detected. Thus, in only 2 days, the 90 to 300 mg Cl/l that these samples had originally contained when they were shipped was no longer present.

PREPARATION OF SAMPLES FOR ANALYSIS

Approximately 1,500 ml of each sample slurry was batch-centrifuged at 1,800 rpm until a clear centrate resulted; this required anywhere from 20 minutes to 6 hours, depending on each sample's unique dewatering characteristics. The clear liquid fraction was carefully decanted into a glass-stoppered bottle and returned to the cold-room. The tightly packed, damp, solid fraction was spread out on a watch glass and air-dried in a hood for at least 3 days.

Each air-dried solid fraction was pulverized and thoroughly macerated with a mortar and pestle. The somewhat fibrous powder was stored in tightly closed, screw-cap vials for subsequent determination of percent total organic chlorine via the Schöniger-flask method.

Eight hundred milliliters of each clear centrate was extracted with three 60-ml portions of 85% hexane-15% diethylether (Burdick and Jackson high-purity solvents were used exclusively throughout this project). The three 60-ml extracts of each centrate were combined and dried overnight with 20 g of anhydrous Na_2SO_4. A separate 180-ml portion of the mixed extraction solvent was also treated with Na_2SO_4; this solvent blank was carried through all subsequent operations, including all analyses involving these extracts. Each dried extract was decanted from the settled Na_2SO_4 through solvent-washed glass wool; the filtrate was collected in a Kuderna-Danish flask fitted with a removable 10-ml graduated thimble. A Snyder condenser was attached to each K-D flask, and the extracts were concentrated on a hot-water bath to about 10 ml. Each extract was further concentrated to a final volume of 0.9 to 1.0 ml by a combination of judicious heating, plus a fine stream of inert gas directed on the surface of the extract. Each K-D thimble was tightly stoppered and refrigerated until its contents could be brought back to a room-temperature volume of 1.0 ml by addition of pure hexane. Each extract was then transferred to a teflon-faced septum vial for subsequent GC/MS study and for determination of total, hexane-ether extractable, non-volatile organic chlorine via microcoulometric titration.

Figure 1 is a line diagram illustrating the sequence of sample preparation steps required before the analyses described as follows.

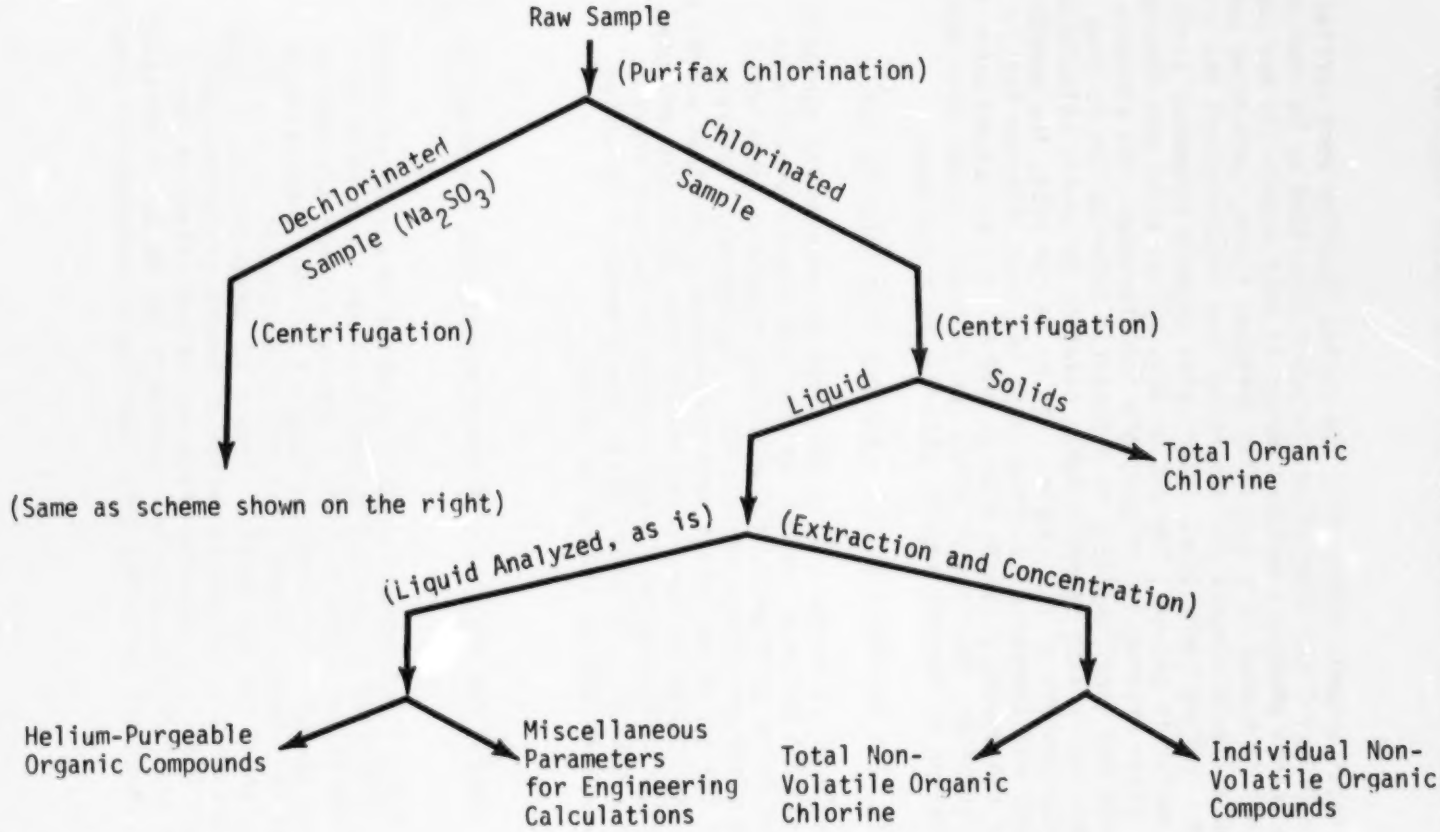

Figure 1. Flow sheet for sample processing and analysis of purifaxed sludges and septage (A "control" portion of raw sample was carried through the same laboratory operations and analyses as shown on the right-hand side of the figure.)

DETERMINATION OF PERCENT TOTAL ORGANIC CHLORINE IN THE SOLIDS FRACTIONS

Procedure

Analyses for total organic chlorine in the solids fraction were carried out using a modified Schöniger-flask combustion procedure described by Welcher and Ma (4). This is a method whereby a weighed amount of each sample (in our case, the air-dried solids) is burned in a specially designed flask, containing pure oxygen and a suitable liquid reagent for absorbing (and neutralizing) the acidic combustion products. During combustion, chlorinated organic compounds yield CO_2, HCl, and (if sulfur is present) SO_2 and/or SO_3, all of which are absorbed as soluble salts. After destruction of possible interferences, the contents of the flask are transferred quantitatively to a beaker. Chloride ion is then titrated potentiometrically with standard $AgNO_3$ solution to permit calculation of the total chlorine content of the sample. If, as in our case, the sample contains both organic and inorganic chlorine (that is, free chloride ion), a separate portion of the unburned sample must be boiled with deionized water to dissolve inorganic chloride; the free chloride ion is then titrated with $AgNO_3$. This permits calculation of percent organic chlorine by difference:

Percent organic Cl = percent total Cl - percent free chloride ion.

Since each sample of air-dried solids contained an unknown and variable concentration of residual moisture, values for percent organic chlorine in air-dried solids had to be correspondingly adjusted; otherwise, meaningful comparisons of data might not have been possible. Accordingly, separate weighed portions of the air-dried solids were oven-dried to constant weight at 105 to 110 C. The percentages of oven-dried solids were calculated and used to adjust the Schoniger values to true organic chlorine (percent organic chlorine based on dry solids). By coincidence, every batch of air-dried solids assayed 95±1%, expressed as oven-dried solids.

Results

The Schöniger results for both sets of air-dried samples are shown in Table 1.

The values in Table 1 for percent organic chlorine in air-dried solids were mathematically converted to the corresponding values for oven-dried solids (Table 2). The values shown in Table 2 are not as insignificant as might appear at first glance. For example, assume that the number-average equivalent weight of chlorinated organics in the solids phases is only 350 (a number that is probably far too small). Then a 1% concentration of total organic chlorine represents a 10% concentration of monochlorinated organic compounds. If a more realistic number-average equivalent weight of 700 is assumed, then 1% of total organic chlorine represents 20% as monochlorinated organic compounds. These are certainly very significant concentration levels.

TABLE 1. PERCENT TOTAL CHLORINE, INORGANIC CHLORIDE, AND ORGANIC CHLORINE IN AIR-DRIED SOLIDS

Parameter	Purifaxed primary/ secondary sludge solids, %	Purifaxed septage solids, %
Total Cl in raw sample	0.09, 0.07	0.15, 0.21
Inorganic Cl in raw sample	Not detectable	0.05, 0.04
Organic Cl in raw sample	0.08	0.14
Total Cl in dechlorinated sample	2.52, 2.59	2.26, 2.28
Inorganic Cl in dechlorinated sample	1.67, 1.67	1.31, 1.28
Organic Cl in dechlorinated sample	0.89	0.97
Total Cl in chlorinated sample	2.64, 2.66	3.00, 2.99
Inorganic Cl in chlorinated sample	1.80, 1.83	2.08, 2.04
Organic Cl in chlorinated sample	0.83	0.94

TABLE 2. PERCENT TOTAL ORGANIC CHLORINE BASED ON OVEN-DRIED SOLIDS

Parameter	Purifaxed primary/ secondary sludge solids, %	Purifaxed septage solids, %
Organic Cl in raw sample	0.08	0.15
Organic Cl in dechlorinated sample	0.94	1.01
Organic Cl in chlorinated sample	0.87	0.98

DETERMINATION OF TOTAL, HEXANE-ETHER EXTRACTABLE, NON-VOLATILE ORGANIC CHLORINE IN THE LIQUID PHASES (i.e., CENTRATES)

Procedure

These analyses were carried out on the 1.0-ml concentrates obtained by hexane-ether extractions of sample centrates. The methodology involves microcombustion of a known volume of sample or extract, followed by microcoulometric titration of the resulting halogen acids (in our case, HCl) with silver ion in a special cell designed for this purpose. The equipment and related procedure is available from the Dohrmann Division of Envirotech Corporation as their microcoulometric titration system, MCTS-20-D. Just before each day's analyses, the equipment is checked and calibrated with a suitable standard solution of a pure organic halogen compound dissolved in iso-octane.

Results

The values for total halogen, expressed as Cl, for both sets of centrates are shown in Table 3.

TABLE 3. PERCENT TOTAL, HEXANE-ETHER EXTRACTABLE, NON-VOLATILE ORGANIC CHLORINE IN THE LIQUID PHASES

	*µg Cl/l of centrate	
Sample centrate	Purifaxed primary/ secondary sludge	Purifaxed septage
Raw sample	0.9	25.4
Dechlorinated sample	73.4	136
Chlorinated sample	134	170

*Each value shown is the average of replicate microcoulometric titrations.

DETERMINATION OF INDIVIDUAL, HELIUM-PURGEABLE, ORGANIC COMPOUNDS IN THE LIQUID PHASES

Procedure

These determinations were carried out by combining the purge-and-trap technique described by Bellar and Lichtenberg (3), with GC/MS detection and analysis of the volatile (trapped-out) organic compounds in each of the liquid phases. A suitable aliquot of liquid sample was purged for 11 min at room temperature with 20 ml/min of helium. The gaseous effluent was passed through a Bellar trap, the first 60% of which was packed with 60/80 mesh Tenax-GC, and the last 40% with Davison grade 15 silica gel. Direction of gas flow was such that the purged organics contacted first the Tenax, then the silica gel. The trapped organics were thermally desorbed for a period of 3 min using a 200 C flash heater on the trap. During this time, the desorbed organics were swept by 20 ml/min of helium into the injection port (200 C) of a Finnigan Model 9500 gas chromatograph equipped with a 1.52-M (5-ft) x 2-mm ID glass column packed with 60/80 mesh Tenax-GC and maintained at a temperature slightly below 50 C. After the trap had been flash-heated for 3 min, temperature programming of the GC column was immediately begun for a 30-min run. Column temperature was increased at a rate of 8°/min from 50 C to 190 C, and it was held at the latter temperature until the 30-min run was over. All during the GC run, automatic data acquisition and display were accomplished with a directly interfaced Finnigan, Model 3300, mass spectrometer system. The mass spectrometer was operated in the electron impact (EI) mode at 70 eV and 10^{-7} amps/volt sensitivity. The chosen mass range was 20 to 260 atomic mass units with 4-sec scans.

Because of pronounced foaming properties of the Purifaxed samples, only well-diluted 1.0-ml aliquots could be analyzed. That is, each 1.0-ml aliquot had to be diluted to 5.0 ml with boiled Milli-Q water before the purge-and-trap step. On the other hand, undiluted 5.0-ml aliquots of both the raw sludge and raw septage could be analyzed with no difficulty, as could 5.0-ml aliquots of calibration standards.

Results

The values for helium-purgeable, volatile organic compounds in raw dechlorinated, and chlorinated samples are listed in Tables 4, 5, and 6, respectively.

DETERMINATION OF INDIVIDUAL, HEXANE-ETHER EXTRACTABLE, NON-VOLATILE ORGANIC COMPOUNDS IN THE LIQUID PHASES

Procedure

The concentrated hexane-ether extracts that had already been analyzed for total non-volatile organic chlorine were further reduced in volume to 0.5 ml each, then analyzed for individual organic compounds via GC/MS. The conditions for each GC/MS analysis were as follows:

TABLE 4. CONCENTRATIONS OF HELIUM-PURGEABLE ORGANIC COMPOUNDS IN BOTH RAW SAMPLES

Trapped volatile compounds	Concentration of compound, µg/l	
	Mixed primary/ secondary sludge	Septage
Methyl chloroform	5	60
Benzene	10	2
Dimethyldisulfide	150	-
Ethanol	-	Not quantified
Acetone	-	Not quantified
Dichloromethane	-	1
1, 1-Dichloroethane	-	60
Chloroform	-	8
Dithiabutane	-	150
Toluene	-	75
Xylenes	-	50
Chlorotoluenes	-	95
Dichlorobenzenes	-	100
Methanethiol	Not quantified	-
2,3,4-Trithiapentane	Not quantified	-

TABLE 5. CONCENTRATIONS OF HELIUM-PURGEABLE ORGANIC COMPOUNDS IN BOTH DECHLORINATED SAMPLES

Trapped volatile compounds	Concentration of Compounds, µg/l	
	Mixed primary/ secondary sludge	Septage
Cyanogen chloride	700	170
Dichloromethane	100	10
Chloroform	100	65
Carbon tetrachloride	30	-
Benzene	5	2
Ethanol	Not quantified	Not quantified
Acetone	Not quantified	Not quantified
3-Methylbutanal	Not quantified	Not quantified
Toluene	2	60
Hexanal	Not quantified	-
Furfural	Not quantified	-
Chloroethane	-	3
1, 1-Dichloroethane	-	85
Methyl chloroform	-	40
Dichloroacetonitrile	-	50
Chlorotoluenes	-	130
Dichlorobenzenes	-	300
n-Valeronitrile	-	Not quantified

TABLE 6. CONCENTRATIONS OF HELIUM-PURGEABLE ORGANIC COMPOUNDS IN BOTH CHLORINATED SAMPLES

Trapped volatile compounds	Concentration of compounds, µg/l	
	Mixed primary/ secondary sludge	Septage
Cyanogen chloride	900	250
Acetone	5	Not quantified
Dichloromethane	100	50
Chloroform	100	120
Toluene	1	60
Benzene	1	10
3-Methylbutanal	Not quantified	-
3-Methylpentanal	Not quantified	-
Chloroethane	-	5
1, 1-Dichloroethane	-	60
Methyl chloroform	-	40
Carbon tetrachloride	-	2
Dichloroacetonitrile	-	60
n-Valeronitrile	-	50
Chlorotoluenes	-	170
Dichlorobenzenes	-	260
Hexane	-	Not quantified

a. Column--1.53-M (5-ft) x 2-mm ID glass column, packed with 3% OV-1 on 80/100 mesh Gas Chrom Q.

b. Flowrate--20 ml/min of helium.

c. Column temperature--3 min at 30 C, followed by programming to 230 C at 8°/min for a total MS run time of 45 min.

d. Mass range--20 to 500 atomic mass units with 4-sec scans (i.e., integration time of 8 milliseconds/atomic mass unit).

e. Sensitivity--10^{-7} amp/volt.

f. Electron energy--70 eV.

g. Real time GC attenuation--3.

h. Data acquisition (the 45-min MS run) was started 1.0 min after injection to eliminate most of the solvent peak.

Compounds identified from EI/MS spectra during this phase of the project were confirmed by running standards (when these were on-hand) or by reruns using the CI/MS side of the Finnigan system. The reported concentrations are accurate to only ±50%, and they are based on the assumption that 100% recovery of each identified compound was realized up to the point of GC/MS analysis.

Results

Tables 7, 8, and 9 show the values found for the individual, hexane-ether extractable, non-volatile organic compounds in raw, dechlorinated, and chlorinated samples, respectively.

DETERMINATION OF ADDITIONAL PARAMETERS FOR VENTURA CENTRATES TO PERMIT COST CALCULATIONS FOR FILTRATION/CARBON ADSORPTION AS AN ADJUNCT TO PURIFAX TREATMENT

Procedure

Each of the three Ventura centrates was analyzed for total dissolved solids, total suspended solids, and total organic carbon by procedures described in Standard Methods for the Examination of Water and Wastewater (5). A separate portion of each centrate was then filtered through a 0.45-μm Millipore membrane, and these filtrates were also analyzed for total organic carbon.

Results

The analytical values for these additional engineering parameters are listed in Table 10.

TABLE 7. CONCENTRATIONS OF HEXANE-ETHER EXTRACTABLE, NON-VOLATILE ORGANIC COMPOUNDS IN BOTH RAW SAMPLES

Extracted compound	Concentration of Compound, µg/l	
	Mixed primary/ secondary sludge	Septage
Diethyl phthalate	2	-
Isobutyl phthalate	80	-
Di-n-butyl phthalate	40	-
Isopropyl phthalate	2	-
Di-(2-ethylhexyl) phthalate	10	-
Farnesol	2	-
Chlorotoluene	-	20
3-hexanone	-	50
Fenchyl alcohol	-	20
Camphor	-	20
Myrcenol	-	150
Isoborneol	-	20
Terpinene-4-ol	-	20
Alpha-terpineol	-	800
Indole	-	20
3-Methylindole	-	30
1,1-Dibutoxyethane	-	30
Ethyl-p, p'-dichlorobenzilate	-	10

TABLE 8. CONCENTRATIONS OF HEXANE-ETHER EXTRACTABLE, NON-VOLATILE ORGANIC COMPOUNDS IN BOTH DECHLORINATED SAMPLES

Extracted compound	Concentration of compound, µg/l	
	Mixed primary/ secondary sludge	Septage
Pentachloroacetone	100	50
Chloroform	10	-
2,4,6-Trichlorophenol	2	-
Diethyl phthalate	2	5
Di-(2-ethylhexyl) phthalate	100	-
Dodecan-6,7-dione	2	-
3,7,7-Trimethyl-bicyclo-(3.1.1)-2-heptanol	5	-
3-Hexanone	Not quantified	-
Acetone	Not quantified	-
Chlorotoluene	-	10
Isovaleric acid	-	20
Dichlorobenzene	-	20
Butyric acid	-	30
(2-chloroethyl)-benzene	-	30
Fenchyl alcohol	-	50
3-Pentanol	-	40
Isoborneol	-	50
2-Ethylbutanoic acid	-	5
Stearic acid	-	150
1,1-Dibutoxyethane	-	30
Toluene	-	Not quantified
Farnesol	5	-

TABLE 9. CONCENTRATIONS OF HEXANE-ETHER EXTRACTABLE, NON-VOLATILE ORGANIC COMPOUNDS IN BOTH CHLORINATED SAMPLES

Extracted compound	Concentration of compound, µg/l	
	Mixed primary/ secondary sludge	Septage
3-Methyl-3-pentanol	2	-
3-Hexanone	30	-
Pentachloroacetone	100	40
Chloroform	30	-
2,4,6-Trichlorophenol	2	-
Diethyl phthalate	2	-
Isobutyl phthalate	80	-
Di-(n-butyl) phthalate	100	-
Di-(2-ethylhexyl) phthalate	2	10
Farnesol	5	-
2-Methyl-3-pentanol	Tentative identification	-
Chlorotoluene	-	10
Dichlorobenzene	—	10
(2-chloroethyl)-benzene	-	20
Fenchyl alcohol	-	30
Camphor	-	30
3-Pentanol	-	30
Iso-borneol	-	30
n-Butyl-n-butyrate	-	20
Stearic acid	-	150
1,1-Dibutoxyethane	-	10
Elemol	-	10
Nerolidol isomer	-	20
Diethylether	-	50

TABLE 10. MISCELLANEOUS ENGINEERING PARAMETERS FOR VENTURA CENTRATES

Centrate parameter	Concentration of parameter, mg/l		
	Raw	Dechlorinated	Chlorinated
Total dissolved solids	1,984	2,855	3,158
Total suspended solids	31.0	21.0	21.0
Total organic carbon	375	200	190
Rerun of total organic carbon after filtration through 0.45-μm millipore membranes	325	175	175

DISCUSSION

Relatively high percentages (1% by weight) of organic chlorine were found in the Purifaxed solids phases. These chlorinated organics represent a significant potential environmental hazard. If these solids phases are disposed of as landfill material, and if subsequent long-term landfill leaching occurs, at least some of these chlorinated organics are sure to re-enter the environment with unknown health-effects risks. Unfortunately, the present state-of-the-art of analytical chemistry does not permit identification of more than a small fraction of the individual chlorinated organic constituents in Purifaxed solids phases. Such solids are extremely insoluble in most organic solvents and therefore resist ordinary extraction methods. Even extractive steam distillation of Purifaxed solids probably would permit isolation and analysis of only small percentages of the chlorinated organics actually present.

Evaluation of all the data on the Purifaxed liquid phases shows that less than 1% of the total organic carbon in these phases were accounted for by recovered chlorinated organic compounds. For example, the centrates from Ventura contained approximately 200 mg/l total organic carbon, and less than 1 mg/l was identified as specific organic compounds. This strongly indicates that recoveries of chlorinated organics before analysis were very low. This result is readily understandable for the following reasons:

a. The microcoulometric titration values obtained for total, hexane-ether extractable, non-volatile organic chlorine in the liquid phases were in turn dependent on the relative fractions of dissolved chlorinated organics extracted (for subsequent analysis) by the solvent mixture employed for this purpose. Had most of the chlorinated organics in the

aqueous phases been highly polar in nature (that is, highly water-soluble), then no simple extraction procedure could have recovered more than a small fraction of the compounds actually present.

b. When the hexane-ether extracts had to be concentrated from 180 ml down to 0.5-1.0 ml for microcoulometric and GC/MS analyses, significant (but unknown) percentages of the extracted chlorinated organics were lost because of volatility. Some of these volatiles obviously would have been accounted for during the independent determinations of helium-purgeable constituents. On the other hand, much of the lost volatile material would not have been thus accounted for, but instead would have completely escaped detection.

Better recovery methods could no doubt be devised, but this would require a major analytical undertaking.

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